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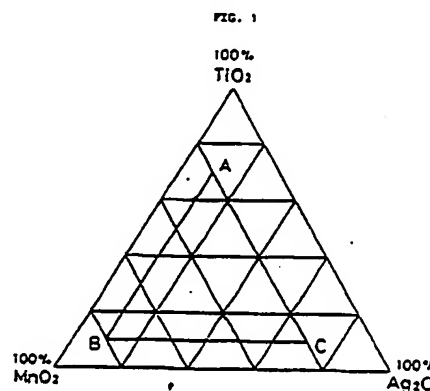
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⑤ Ozone decomposition catalyst and method.

⑦ A catalyst for ozone decomposition which comprises:  
at least one oxide of a metal selected from the group consisting of Cu, Mn, Co, Fe and Ni; and at least one oxide of a metal selected from the group consisting of Ti and Ag, and/or Au.

Such a catalyst free from deterioration in activity even when it is used under severe conditions, comprises: a ternary metal oxide represented by the formula of  $x\text{MnO}_2 \cdot y\text{Ag}_2\text{O} \cdot z\text{TiO}_2$  wherein weight proportion coordinates (x, y, z) of the oxide on a triangular diagram are either on sides of a triangle formed by connecting three points (20, 10, 70), (80, 10, 30) and (20, 70, 10) with straight lines or within the triangle, as seen in Fig. 1.



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## OZONE DECOMPOSITION CATALYST AND METHOD

This invention relates to a catalyst for decomposing ozone (contained, for example, in the air).

There have been proposed various methods of decomposing noxious ozone contained in the air - for example adsorption using a porous material such as activated carbon or zeolite, or oxidative decomposition using a catalyst such as  $\text{MnO}_2$ .

5 However, these methods are not satisfactory. The adsorption method has the disadvantage that the adsorbant must be regenerated; moreover, maintenance of the ozone removing equipment requires much labor and expense. Oxidative decomposition has no such disadvantages, but the known catalysts have insufficient activity; we have investigated the durability of a variety of ozone decomposing catalysts, and found that in general catalysts deteriorate markedly in activity when they are used under severe conditions  
10 of high ozone concentration with large area velocity.

The present invention provides a catalyst for decomposing ozone which comprises at least one metal oxide selected from those of Cu, Mn, Co, Fe and Ni and at least one metal oxide of selected from those of Ti and Ag, and/or Au.

Such catalysts may be exemplified by binary catalysts such as  $\text{MnO}_2\text{-TiO}_2$ ,  $\text{CuO-TiO}_2$ ,  $\text{Co}_3\text{O}_4\text{-TiO}_2$ ,  
15  $\text{Fe}_2\text{O}_3\text{-TiO}_2$  or  $\text{Fe}_2\text{O}_3\text{-Au}$ , and ternary catalysts such as  $\text{MnO}_2\text{-Co}_3\text{O}_4\text{-TiO}_2$ ,  $\text{MnO}_2\text{-Co}_3\text{O}_4\text{-Ag}_2\text{O}$ ,  $\text{MnO}_2\text{-Ag}_2\text{O-TiO}_2$  or  $\text{NiO-MnO}_2\text{-TiO}_2$ .

The active components are composed of at least one oxide of metal selected from Cu, Mn, Co, Fe and Ni (preferably in amounts of 5-75 wt.% as metals in total) and at least one oxide of metal selected from Ti and Ag, and/or Au, preferably in amounts of 25-95 wt.% as metals.

20 The catalyst is not limited to any specific form, and for example may be in the form of honeycombs, pellets, cylinders, plates or pipes.

The catalyst preferably contains the active components in amounts of not less than 50 wt.%, more preferably in amounts of not less than 75 wt.%.

The catalyst may be produced by any known methods such as impregnating, kneading, coprecipitating,  
25 precipitating or oxide admixing methods. In the production of the catalyst, there may be used molding assistants to provide plasticity with the active component used, reinforcements such as inorganic fibers to increase mechanical strength of the catalyst obtained, or organic binders.

The ozone decomposition is best carried out at temperatures of 0-40 °C, preferably of 10-30 °C. When  
30 the reaction temperature is less than 0 °C, the reaction velocity may be too slow, whereas when more than 40°C, heat energy is needed and this is undesirable from the standpoint of energy economy.

A gas which contains ozone is best contacted with the catalyst at an area velocity of 5-50, wherein the area velocity is the space velocity ( $\text{hr}^{-1}$ ) divided by gas contact area per unit volume ( $\text{m}^2/\text{m}^3$ ) of the catalyst. When the area velocity is less than 5, an undesirably large volume of catalyst may be needed  
whereas when it is over 50, the ozone decomposition rate may be too low.

35 When ozone is decomposed under mild conditions of a small CA value (which is the product of ozone concentration at the reactor inlet and area velocity), there is substantially no deterioration of the catalyst. However, many catalysts rapidly deteriorate when the reaction is carried out under severe conditions of a CA value of not less than 30.

We have found that among the ozone decomposing catalysts of the invention, a ternary catalyst mainly  
40 composed of  $\text{MnO}_2\text{-Ag}_2\text{O-TiO}_2$  of specific weight proportions is the most durable.

The preferred ozone decomposing catalyst contains a ternary metal oxide of formula  $x\text{MnO}_2\cdot y\text{Ag}_2\text{O}\cdot z\text{TiO}_2$  wherein weight proportion coordinates (x, y, z) of the oxide on a triangular diagram are either on sides of a triangle formed by connecting three points (20, 10, 70), (80, 10, 30) and (20, 70, 10) with  
45 straight line or within the triangle, as illustrated in Fig. 1. This catalyst of the invention does not deteriorate under severe conditions of a CA value of not less than 30.

The catalyst of the invention may further contain at least one metal selected from Pt, Ru, Re, Os, Rh, Ir and Pd, or an oxide thereof, and/or Au.

The invention will now be described in more detail with reference to Examples; however, the invention is not limited thereto. Reference will also be made to the accompanying drawings, in which :

50 FIGURE 1 is a triangular diagram which illustrates the compositions of preferred ozone decomposition catalysts of the invention; and

FIGURE 2 is a flow sheet for measurement of catalyst activity.

## A. Preparation of Catalysts

Example 1

704 g of  $\text{MnO}_2$  having a specific surface area of  $48 \text{ m}^2/\text{g}$  and 250 g of glass beads were added to 1034 ml of titania sol ( $\text{TiO}_2$  content: 150 g/l), and the resultant mixture was stirred over 30 minutes to provide a slurry.

The slurry was impregnated into a honeycomb formed with corrugates of ceramic fibers having a porosity of 81 % and a pitch of 4.0 mm to provide a binary catalyst having  $\text{MnO}_2\text{-TiO}_2$  (82/18 in weight ratio) supported on the honeycomb in a support ratio of 85 %; the support ratio is the weight of the active components supported on the honeycomb divided by the weight of the honeycomb.

Example 2

30 g of  $\text{MnO}_2$  having a specific surface area of  $48 \text{ m}^2/\text{g}$  and 70 g of anatase  $\text{TiO}_2$  having a specific surface area of  $85 \text{ m}^2/\text{g}$  were added to 170 ml of titania sol ( $\text{TiO}_2$  content: 150 g/l), and the resultant mixture was stirred over 30 minutes to provide a slurry.

The slurry was impregnated into the same honeycomb as in Example 1 to provide a binary catalyst having  $\text{MnO}_2\text{-TiO}_2$  (24/76 in weight ratio) supported thereon in a support ratio of 101 %.

Example 3

$\text{CuO}$  having a specific surface area of  $62 \text{ m}^2/\text{g}$  was used in place of the  $\text{MnO}_2$  in Example 2; a binary catalyst was prepared which had  $\text{CuO-TiO}_2$  (24/76 in weight ratio) supported thereon in a support ratio of 91 %.

Example 4

$\text{Co}_3\text{O}_4$  having a specific surface area of  $53 \text{ m}^2/\text{g}$  was used in place of the  $\text{MnO}_2$  in Example 2; a binary catalyst was prepared which had  $\text{Co}_3\text{O}_4\text{-TiO}_2$  (24/76 in weight ratio) supported thereon in a support ratio of 91 %.

Example 5

$\text{Fe}_2\text{O}_3$  having a specific surface area of  $53 \text{ m}^2/\text{g}$  was used in place of the  $\text{MnO}_2$  in Example 2; a binary catalyst was prepared which had  $\text{Fe}_2\text{O}_3\text{-TiO}_2$  (24/76 in weight ratio) supported thereon in a support ratio of 78 %.

Example 6

500 ml of an aqueous solution of 112 g of manganese acetate (tetrahydrate), 182 g of cobaltous nitrate (hexahydrate) and 63 g of metatitanic acid ( $\text{TiO}_2$  content: 40 %) was prepared. Ammonia water was gradually added to the solution under stirring to neutralize the solution to a pH of 7.0, whereupon slurry precipitates were formed.

The slurry was impregnated into the same corrugated honeycomb as in Example 1, and the honeycomb was calcined at a temperature of  $450^\circ\text{C}$  for three hours, to provide a ternary catalyst having  $\text{MnO}_2\text{-Co}_3\text{O}_4\text{-TiO}_2$  (25/50/25 in weight ratio) supported thereon in a support ratio of 89 % and a specific surface area of  $72 \text{ m}^2/\text{g}$ .

Example 7

500 ml of an aqueous solution of 17.8 g of manganese acetate (tetrahydrate), 282 g of cobaltous nitrate (hexahydrate) and 1.5 g of silver nitrate was prepared. An aqueous solution of ammonium carbonate was gradually added to the solution under stirring to neutralize the solution to a pH of 7.0, whereupon slurry precipitates were formed.

- 5 The slurry was impregnated into the same honeycomb as in Example 1, and the honeycomb was calcined at a temperature of 450° C for three hours, to provide a ternary catalyst having  $\text{Co}_3\text{O}_4\text{-MnO}_2\text{-Ag}_2\text{O}$  (20/40/1 in weight ratio) supported thereon in a support ratio of 92 % and a specific surface area of 65 m<sup>2</sup>/g.

#### 10 Example 8

500 ml of an aqueous solution of 74.4 g of cupric nitrate (hexahydrate), 17.8 g of manganese acetate (tetrahydrate) and 1.5 g of silver nitrate was prepared. An aqueous solution of ammonium carbonate was gradually added to the solution under stirring to neutralize the solution of a pH of 7.0, whereupon slurry precipitates were formed.

- 15 The slurry was impregnated into the same honeycomb as in Example 1, and the honeycomb was calcined at a temperature of 450° C for three hours, to provide a ternary catalyst having  $\text{CuO-MnO}_2\text{-Ag}_2\text{O}$  (20/40/1 in weight ratio) supported thereon in a support ratio of 87 % and a specific surface area of 71 m<sup>2</sup>/g.

20

#### Example 9

500 ml of an aqueous solution of 112 g of manganese acetate (tetrahydrate), 195 g of nickel nitrate (hexahydrate) and 63 g of metatitanic acid ( $\text{TiO}_2$  content: 40 %) was prepared. Ammonia water was gradually added to the solution under stirring to neutralize the solution to a pH of 7.0; whereupon slurry precipitates were formed.

- 25 The slurry was impregnated into the same honeycomb as in Example 1, and the honeycomb was calcined at a temperature of 450° C for three hours, to provide a ternary catalyst having  $\text{MnO}_2\text{-NiO-TiO}_2$  - (25/50/25 in weight ratio) supported thereon in a support ratio of 94 % and a specific surface area of 80 m<sup>2</sup>/g.

30

#### Reference Example 1

35 30 g of  $\text{MnO}_2$  having a specific surface area of 48 m<sup>2</sup>/g and 70 g of a mixture of titanium tetrachloride and silica sol (1/1 in a weight ratio as  $\text{TiO}_2/\text{SiO}_2$ ) were mixed together with stirring while ammonia gas was blown thereinto to neutralize the mixture and provide slurry precipitates.

- After fully washing with water, the precipitate was calcined at a temperature of 500° C for three hours, to provide a binary catalyst composed of  $\text{TiO}_2\text{-SiO}_2$  of a specific surface area of 162 m<sup>2</sup>/g.

40

#### Example 10

250 g of manganese dioxide ( $\text{MnO}_2$ ) and 103g of silver oxide ( $\text{Ag}_2\text{O}$ ) were added to 1034 ml of titania sol ( $\text{TiO}_2$  content: 150 g/l). There were further added thereto 250 g of glass beads, and the mixture was stirred to form slurry precipitates.

- The slurry was impregnated into the same honeycomb as in Example 1, to provide a ternary catalyst having  $\text{MnO}_2\text{-Ag}_2\text{O-TiO}_2$  (50/20/30 in weight ratio) supported thereon in a support ratio of 101 %.

50

#### Example 11

1034 ml of titania sol, 155 g of manganese dioxide, 207 g of silver oxide and 250 g of glass beads were used as in Example 10 to give a ternary catalyst having  $\text{MnO}_2\text{-Ag}_2\text{O-TiO}_2$  (30/40/30 in weight ratio) supported thereon in a support ratio of 98 %.

55

#### Example 12

2411 ml of titania sol, 103 g of manganese dioxide, 52 g of silver oxide and 250 g of glass beads were used as in Example 10 to give a ternary catalyst which had  $\text{MnO}_2\text{-Ag}_2\text{O-TiO}_2$  (20/10/70 in weight ratio) supported thereon in a support ratio of 105 %.

5

#### Example 13

1034 ml of titania sol, 1240 g of manganese dioxide, 155 g of silver oxide and 250 g of glass beads were used as in Example 10 to give a ternary catalyst which had  $\text{MnO}_2\text{-Ag}_2\text{O-TiO}_2$  (80/10/10 in weight ratio) supported thereon in a support ratio of 101 %.

10

#### Example 14

1034 ml of titania sol, 310 g of manganese dioxide, 1085 g of silver oxide and 250 g of glass beads were used as in Example 10 to give a ternary catalyst which had  $\text{MnO}_2\text{-Ag}_2\text{O-TiO}_2$  (20/70/10 in weight ratio) supported thereon in a support ratio of 103 %.

15

#### Example 15

1034 ml of titania sol, 78 g of manganese dioxide, 155 g of silver oxide and 250 g of glass beads were used as in Example 10 to give a ternary catalyst which had  $\text{MnO}_2\text{-Ag}_2\text{O-TiO}_2$  (20/40/40 in weight ratio) supported thereon in a support ratio of 99 %.

20

25

#### Example 16

1034 ml of titania sol, 194 g of manganese dioxide, 39 g of silver oxide and 250 g of glass beads were used as in Example 10 to give a ternary catalyst which had  $\text{MnO}_2\text{-Ag}_2\text{O-TiO}_2$  (50/10/40 in weight ratio) supported thereon in a support ratio of 95 %.

30

#### Example 17

1034 ml of titania sol, 775 g of manganese dioxide, 620 g of silver oxide and 250 g of glass beads were used as in Example 10 to give a ternary catalyst which had  $\text{MnO}_2\text{-Ag}_2\text{O-TiO}_2$  (50/40/10 in weight ratio) supported thereon in a support ratio of 102 %.

35

40

#### Example 18

1034 ml of titania sol, 465 g of manganese dioxide, 155 g of silver oxide and 250 g of glass beads were used as in Example 10 to give a ternary catalyst which had  $\text{MnO}_2\text{-Ag}_2\text{O-TiO}_2$  (60/20/20 in weight ratio) supported thereon in a support ratio of 102 %.

45

#### Reference Example 2

1034 ml of titania sol, 52 g of manganese dioxide, 310 g of silver oxide and 250 g of glass beads were used as in Example 10 to give a ternary catalyst which had  $\text{MnO}_2\text{-Ag}_2\text{O-TiO}_2$  (10/60/30 in weight ratio) supported thereon in a support ratio of 98 %.

50

#### Reference Example 3

1034 ml of titania sol, 90 g of manganese dioxide, 13 g of silver oxide and 250 g of glass beads were used as in Example 10 to give a ternary catalyst which had  $\text{MnO}_2\text{-Ag}_2\text{O-TiO}_2$  (35/5/60 in weight ratio)

55

supported thereon in a support ratio of 100 %.

Reference Example 4

5

1034 ml of titania sol, 1395 g of manganese dioxide, 1550 g of silver oxide and 250 g of glass beads were used as in Example 10 to give a ternary catalyst which had  $\text{MnO}_2\text{-Ag}_2\text{O-TiO}_2$  (45/50/5 in weight ratio) supported thereon.

10

Example 19

The ternary catalyst (water absorption: 39.0 %) prepared in Example 10 was immersed in an aqueous solution of chloroplatinic acid (Pt content: 2.56 g/l). After removal of excess solution therefrom, the catalyst  
15 was air dried at normal temperature. Then the catalyst was dried at a temperature of 100°C over eight hours, and then calcined at a temperature of 500°C for three hours, to provide a four component catalyst containing platinum in amounts of 0.1 % by weight in terms of metallic platinum.

20 Example 20

An aqueous solution of ruthenium trichloride (Ru content: 2.56 g/l) was used in place of the aqueous solution of chloroplatinic acid in Example 19 to give a four component catalyst containing ruthenium in amounts of 0.1 % by weight in terms of metallic ruthenium.

25

Example 21

An aqueous solution of rhenium trichloride (Re content: 2.56 g/l) was used in place of the aqueous  
30 solution of chloroplatinic acid in Example 19 to give a four component catalyst containing rhenium in amounts of 0.1 % by weight in terms of metallic rhenium.

Example 22

35

An aqueous solution of osmium trichloride (Os content: 2.56 g/l) was used in place of the aqueous solution of chloroplatinic acid in Example 19 to give a four component catalyst containing osmium in amounts of 0.1 % by weight in terms of metallic osmium.

40

Example 23

An aqueous solution of rhodium trichloride (Rh content: 2.56 g/l) was used in place of the aqueous solution of chloroplatinic acid in Example 19 to give a four component catalyst containing rhodium in  
45 amounts of 0.1 % by weight in terms of metallic rhodium.

Example 24

50 An aqueous solution of iridium tetrachloride (Ir content: 2.56 g/l) was used in place of the aqueous solution of chloroplatinic acid in Example 19 to give a four component catalyst containing iridium in amounts of 0.1 % by weight in terms of metallic iridium.

55 Example 25

An aqueous solution of palladium dichloride (Pd content: 2.56 g/l) was used in place of the aqueous solution of chloroplatinic acid in Example 19 to give a four component catalyst containing palladium in

amounts of 0.1 % by weight in terms of metallic palladium.

#### Example 26

An aqueous solution of auric chloride (Au content: 2.56 g/l) was used in place of the aqueous solution of chloroplatinic acid in Example 19 to give a four component catalyst containing gold in amounts of 0.1 % by weight in terms of metallic gold.

#### Reference Example 5

The ternary catalyst (water absorption: 41.0 %) prepared in Reference Example 2 was immersed in an aqueous solution of chloroplatinic acid (Pt content: 2.44 g/l). After removal of excess solution therefrom, the catalyst was air dried at normal temperature. Then the catalyst was dried at a temperature of 100 °C over eight hours, and then calcined at a temperature of 500 °C for three hours, to provide a four component catalyst containing platinum in amounts of 0.1 % by weight in terms of metallic platinum.

#### B. Measurement of Catalyst Activity

The activity of the catalysts prepared in Examples 1-26 and Reference Examples 1-5 was measured in accordance with the flow sheet shown in Fig. 2, in which 1 designates an ozone generator, into which air is introduced to generate ozone in an appropriate concentration. The air containing ozone is then sent to a catalyst reactor 2. The ozone concentration in the air is determined with an ozone analyzer 3 at the inlet and outlet of the reactor. Ozone decomposition rate (%) is calculated as [(ozone concentration at inlet - ozone concentration at outlet)/ozone concentration at inlet] x 100.

The reaction conditions were as follows:

Space velocity: 20000 hr<sup>-1</sup>  
Temperature: 20 °C

In the measurement with the catalysts of Examples 10-26 and Reference Examples 2-5, ozone concentration at the inlet of the reactor and area velocity were varied so that CA values were 10, 30 and 50, and the ozone decomposition rate was measured at the initial stage, after one hour and two hours, to evaluate durability of the catalyst.

The results are shown in Tables 1-7.

Table 1

	Catalysts	Compositions (Weight Ratio)	Ozone Decomposition Rate (%)
Example 1	MnO <sub>2</sub> /TiO <sub>2</sub>	82/18	96.6
Example 2	MnO <sub>2</sub> /TiO <sub>2</sub>	24/76	92.2
Example 3	CuO/TiO <sub>2</sub>	24/76	96.5
Example 4	Co <sub>3</sub> O <sub>4</sub> /TiO <sub>2</sub>	24/76	93.2
Example 5	Fe <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	24/76	90.6
Example 6	MnO <sub>2</sub> /Co <sub>3</sub> O <sub>4</sub> /TiO <sub>2</sub>	25/50/25	99.8
Example 7	Co <sub>3</sub> O <sub>4</sub> /MnO <sub>2</sub> /Ag <sub>2</sub> O	20/40/1	100.0
Example 8	CuO/MnO <sub>2</sub> /Ag <sub>2</sub> O	20/40/1	100.0
Example 9	MnO <sub>2</sub> /NiO/TiO <sub>2</sub>	25/50/25	92.9
Reference 1	MnO <sub>2</sub> /SiO <sub>2</sub> /TiO <sub>2</sub>	30/35/35	86.8

As apparent from Table 1, the catalysts prepared in Examples 1-9 have higher ozone decomposition rates than those prepared in Reference Example 1.

Further, as apparent from Tables 2-7, the catalysts prepared in Examples 10-26 do not deteriorate

under the conditions of CA values either of 10, 30 or 50; the catalysts prepared in Reference Examples 2-5, wherein the proportions of the active components are not as preferred for the invention, deteriorate under the conditions of CA values of not less than 30, though not under the conditions of a CA value of 10.

Table 2

	Reaction Conditions			Ozone Decomposition Rate		
	CA*	Ozone Concentration at Inlet (ppm)	Area Velocity (m <sup>3</sup> /m <sup>2</sup> ·hr)	Initial	After	
					1 hour (%)	2 hours
Example 10	10	1	10	100	100	100
		5	2	100	100	100
		10	1	100	100	100
	30	1	30	93.3	93.3	93.3
		5	6	100	100	100
		10	3	100	100	100
	50	1	50	80.3	80.1	80.1
		5	10	100	100	100
		10	5	100	100	100
Example 11	10	1	10	100	100	100
		5	2	100	100	100
		10	1	100	100	100
	30	1	30	90.9	90.8	90.7
		5	6	100	100	100
		10	3	100	100	100
	50	1	50	76.3	76.1	76.0
		5	10	99.9	100	99.8
		10	5	100	100	100

\* (ppm · m<sup>3</sup>/m<sup>2</sup> · hr)



Table 3

	Reaction Conditions			Ozone Decomposition Rate		
	CA*	Ozone Concentration at Inlet (ppm)	Area Velocity (m <sup>3</sup> /m <sup>2</sup> ·hr)	Initial	After	
					1 hour (%)	2 hours
Example 12	30	1	30	86.4	86.3	86.3
		5	6	94.7	94.8	94.8
		10	3	95.2	95.1	95.1
Example 13	30	1	30	92.5	92.5	92.3
		5	6	98.6	98.5	98.5
		10	3	97.8	97.9	97.8
Example 14	30	1	30	83.7	83.6	83.6
		5	6	93.9	93.9	94.0
		10	3	94.2	94.3	94.2
Example 15	30	1	30	82.3	82.3	82.3
		5	6	93.8	93.8	93.8
		10	3	93.5	93.4	93.4
Example 16	30	1	30	92.5	92.4	92.4
		5	6	98.1	97.9	97.9
		10	3	97.6	97.8	97.7
Example 17	30	1	30	93.3	93.2	93.0
		5	6	98.9	98.9	98.9
		10	3	98.3	98.2	98.2

\* (ppm · m<sup>3</sup>/m<sup>2</sup> · hr)

Table 4

	Reaction Conditions			Ozone Decomposition Rate		
	CA*	Ozone Concentration at Inlet (ppm)	Area Velocity (m <sup>3</sup> /m <sup>2</sup> *hr)	Initial	After	
					1 hour (%)	2 hours
Example 18	30	1	30	94.2	94.1	94.1
		5	6	98.6	98.5	98.5
		10	3	98.9	98.8	98.8
Example 19	30	1	30	95.5	95.5	95.4
		5	6	99.4	99.3	99.3
		10	3	99.3	99.3	99.3
Example 20	30	1	30	97.1	96.9	96.9
		5	6	99.3	99.3	99.3
		10	3	99.5	99.4	99.5
Example 21	30	1	30	97.1	97.0	97.1
		5	6	99.5	99.5	99.5
		10	3	99.3	99.3	99.2
Example 22	30	1	30	95.5	95.5	95.5
		5	6	99.3	99.1	99.1
		10	3	99.2	99.2	99.2
Example 23	30	1	30	96.7	96.5	96.5
		5	6	99.6	99.6	99.6
		10	3	99.5	99.5	99.5

\* (ppm \* m<sup>3</sup>/m<sup>2</sup>\*hr)

Table 5

	Reaction Conditions			Ozone Decomposition Rate		
	CA*	Ozone Concentration at Inlet (ppm)	Area Velocity (m <sup>3</sup> /m <sup>2</sup> *hr)	Initial	After	
					1 hour (%)	2 hours
Example 24	30	1	30	96.3	96.2	96.2
		5	6	99.3	99.2	99.2
		10	3	99.5	99.2	99.2
Example 25	30	1	30	95.2	95.1	95.2
		5	6	99.2	99.0	99.0
		10	3	99.4	99.2	99.2
Example 26	30	1	30	97.1	97.0	97.0
		5	6	99.6	99.6	99.6
		10	3	99.5	99.4	99.4
Reference 2	10	1	10	99.9	86.8	71.1
		5	2	100	100	99.8
		10	1	100	100	100
	30	1	30	90.0	49.1	33.9
		5	6	100	96.9	87.4
		10	3	100	99.9	98.4
	50	1	50	74.9	33.3	22.0
		5	10	99.9	86.8	71.1
		10	5	100	98.3	91.7

\* (ppm \* m<sup>3</sup>/m<sup>2</sup>\*hr)

Table 6

	Reaction Conditions			Ozone Decomposition Rate		
	CA*	Ozone Concentration at Inlet (ppm)	Area Velocity ( $\text{m}^3/\text{m}^2 \cdot \text{hr}$ )	Initial	After	
					1 hour (%)	2 hours
Reference 3	10	1	10	99.8	70.9	57.1
		5	2	100	99.8	98.6
		10	1	100	100	100
	30	1	30	87.0	33.7	25.6
		5	6	100	87.2	75.6
		10	3	100	98.4	94.1
	50	1	50	70.6	21.9	15.6
		5	10	99.8	70.9	57.1
		10	5	100	91.5	81.6
Reference 4	10	1	10	99.9	85.9	73.9
		5	2	100	100	99.9
		10	1	100	100	100
	30	1	30	89.1	47.9	36.1
		5	6	100	96.2	89.3
		10	3	100	99.9	98.9
	50	1	50	73.6	32.4	23.5
		5	10	99.9	85.9	73.9
		10	5	100	98.0	93.2

\* ( $\text{ppm} \cdot \text{m}^3/\text{m}^2 \cdot \text{hr}$ )

Table 7

	Reaction Conditions			Ozone Decomposition Rate		
	CA*	Ozone Concentration at Inlet (ppm)	Area Velocity ( $\text{m}^3/\text{m}^2 \cdot \text{hr}$ )	Initial	After	
					1 hour (%)	2 hours
Reference 5	10	1	10	100	88.4	74.4
		5	2	100	100	99.9
		10	1	100	100	100
	30	1	30	94.2	51.2	36.5
		5	6	100	97.2	89.7
		10	3	100	99.9	98.9

\* ( $\text{ppm} \cdot \text{m}^3/\text{m}^2 \cdot \text{hr}$ )

## Claims

1. A catalyst for ozone decomposition which comprises at least one metal oxide selected from those of (a) Cu, Mn, Co, Fe and Ni and at least one metal oxide selected from those of (b) Ti, Ag, and Au.
- 5 2. A catalyst according to claim wherein the metal content of (a) is from 5-75 wt.% of the total metal content of (a) + (b) and the metal content of (b) is from 25 to 95 wt.% of said total.
3. A catalyst for ozone decomposition which comprises a ternary metal oxide of formula  $x\text{MnO}_2 \cdot y\text{Ag}_2\text{O} \cdot z\text{TiO}_2$  wherein weight proportion co-ordinates (x, y, z) of the oxide on a triangular diagram are either on sides of or within a triangle formed by connecting three points (20, 10, 70), (80, 10, 30) and  
 10 (20, 70, 10) with straight lines, as shown in Fig.1..
4. A catalyst according to any of claims 1 to 3 containing at most 50 wt.%, preferably at least 75 wt.%, of said metal oxide(s).
5. A method of decomposing ozone which comprises contacting it with catalyst according to any of claims 1 to 4.
- 15 6. A method according to claim 5 conducted at 0-40 °C.
7. A method according to claim 5 or 6 conducted at an area velocity of 5 to 50.

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FIG. 1

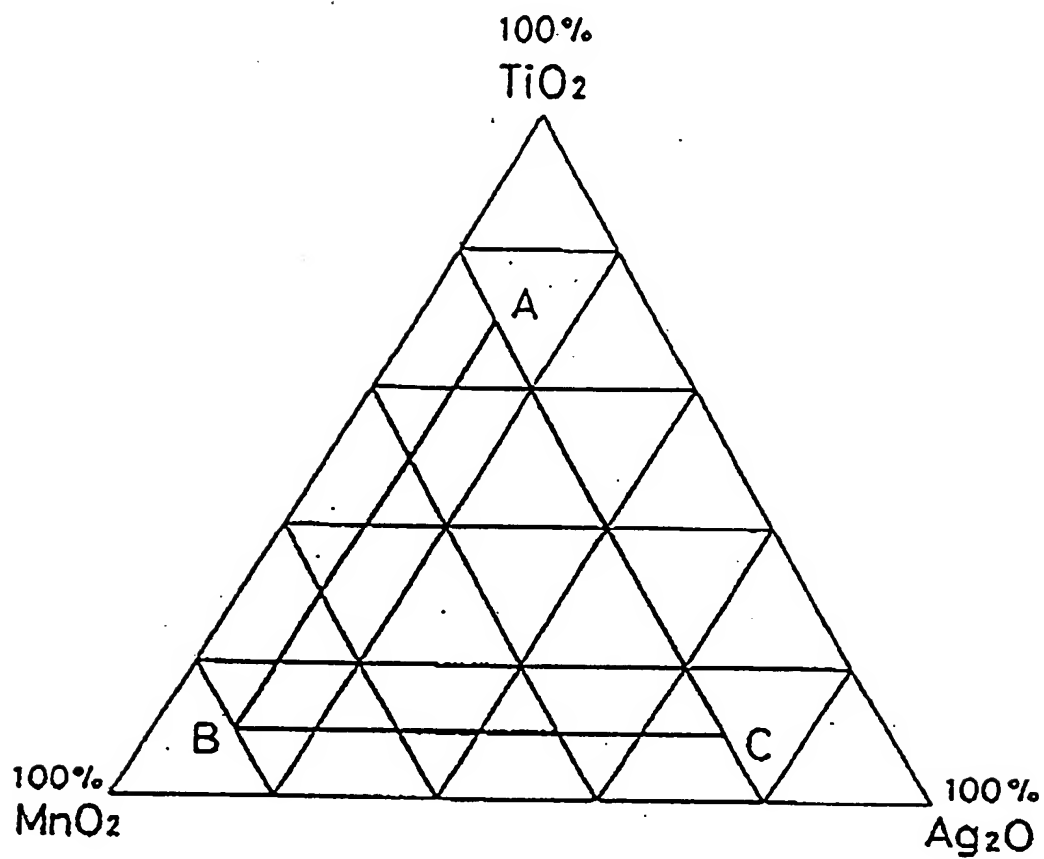
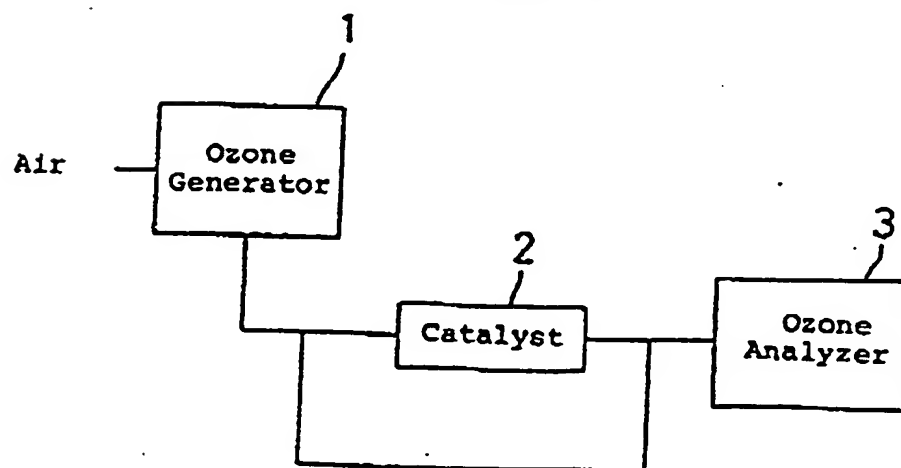


FIG. 2





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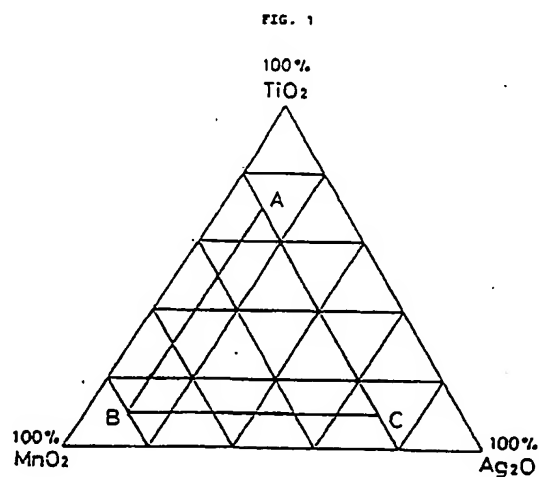
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(54) Ozone decomposition catalyst and method.

(57) A catalyst for ozone decomposition which comprises:

at least one oxide of a metal selected from the group consisting of Cu, Mn, Co, Fe and Ni; and at least one oxide of a metal selected from the group consisting of Ti and Ag, and/or Au.

Such a catalyst free from deterioration in activity even when it is used under severe conditions, comprises: a ternary metal oxide represented by the formula of  $x\text{MnO}_2 \cdot y\text{Ag}_2\text{O} \cdot z\text{TiO}_2$  wherein weight proportion coordinates (x, y, z) of the oxide on a triangular diagram are either on sides of a triangle formed by connecting three points (20, 10, 70), (80, 10, 30) and (20, 70, 10) with straight lines or within the triangle, as seen in Fig. 1.



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# EUROPEAN SEARCH REPORT

Application Number

EP 89 31 1261

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-275620 (NIPPON SHOKUBAI KAGAKU KOGYO) * claims 1-4, 11 *	1-6	801053/36
A	FR-A-2321900 (INSTITUT FIZICHESKOI KHIMI IMENI L.V. PISARZHEVSKOGO AKADEMII) * claims 1-3 *	1, 5-7	
A	DE-A-3003793 (JOH.A. BENCKISER GMBH) * claims 1, 2 *	1	
A	EP-A-257307 (SAKAI CHEMICAL INDUSTRY CO.) * claims 1, 4 *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			8010 801J
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 03 DECEMBER 1990	Examiner BERTRAM H. E. H.
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